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(54) Sensor for volatile materials and gases

(57) A sensor capable of distinguishing between different optical isomers (enantiomers), which sensor comprises a pair of spaced-apart contacts ((14) and a semi-conductive polymer material (20) spanning the gap (15) between the contacts, which polymer material

includes chiral sites. The chiral sites in the polymer material are preferably formed by incorporating an optically active counterion into the polymer material. for example by growing the polymer in the presence of such a counterion. e.g. camphor sulphonic acid.

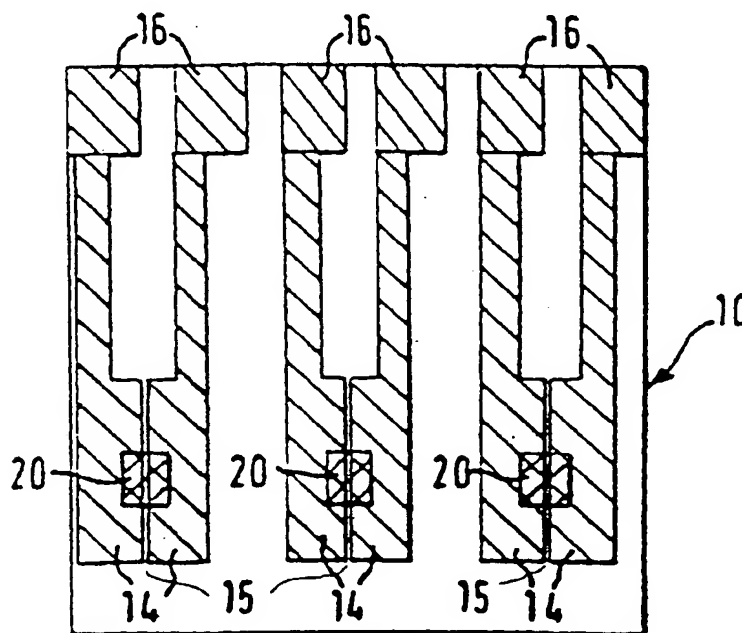


FIG. 7

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Description

Technical Field

The present invention relates to the sensing of gases, volatile materials and in particular to the sensing of smells, aromas or odours.

Background Art

It is known that the smell of certain naturally occurring volatile materials, as perceived by the human nose, is dependent upon the optical activity of the volatile material. For example, d-carvone smells of caraway and dill while the corresponding l-carvone smells of spearmint. It is thus highly desirable to be able to distinguish between different optical isomers (enantiomers). However, optical isomers have identical physical properties to each other and it is therefore difficult to tell the isomers apart using simple analytical techniques without separating out the individual isomers and no such simple technique has hitherto been able to achieve this.

Although optically active aroma materials can be produced synthetically, synthetic production generally produces a racemic mixture of the isomers and the separation of the racemic mixture into its constituent isomers is very expensive. The aroma effect of the racemic mixture is often different from that of the naturally occurring isomer. On the other hand, synthetically produced racemic aroma materials are much cheaper than their naturally occurring counterparts.

It is possible, in order to save costs, to incorporate a limited amount of the synthetic material in with the naturally-occurring material without a significantly noticeable effect on the overall aroma but there is a limit to how much synthetic material can be incorporated before it does have a noticeable effect. For example, l-menthol is added to toothpaste to give it a peppermint flavour. l-menthol is naturally occurring but it can also be produced synthetically in a racemic mixture. The racemic mixture of d- and l- isomers is much cheaper than the naturally occurring l-menthol but, as stated, there is a limit on how much synthetic menthol can be added before the user notices. It is therefore highly desirable to be able to detect the difference between synthetic and naturally occurring menthol to control the amounts of the natural and synthetic menthol added to toothpaste.

The present invention provides a simple sensor that is capable of producing a signal that distinguishes between different enantiomers.

It is known from GB-2176901, GB-2221761, WO93/03355 and WO86/01599 to make sensors for sensing the presence of volatile materials, e.g. smells, aromas and odours, in a gaseous atmosphere. Such sensors consist of a pair of spaced-apart electrical contacts and a semi-conductive polymer spanning the gap between the contacts. The resistance of the polymer changes on exposure to a volatile material, the magni-

tude of the resistance change depending firstly on the nature and amount of the volatile material and secondly on the nature of the polymer.

It is also known to provide a sensing head for analysing a volatile material that comprises an array of such sensors, each containing a different polymer. The different polymers in the sensors of the head respond differently to the presence of a volatile material, e.g. an aroma, in the atmosphere being monitored. The resistance of the polymers of the various sensors sensor head are monitored to give an output signal for each sensor, which may, in effect, be a plot of the resistance of the polymer of each sensor against time. The combination of signals from the various sensors gives a pattern that is characteristic of the aroma concerned and the pattern of sensor signals for a given aroma is often referred to as a "fingerprint" of that aroma. The combination of sensor signals obtained on exposure of the sensor head to a volatile material can be used to detect, characterise and identify the smell, aroma or odour.

The sensors are made by laying down on a substrate a pair of spaced-apart contacts and the polymer is grown (polymerised) electrolytically in the gap between the contacts by dipping the spaced-apart contacts into a monomer solution that also contains a counter ion and a solvent. When an electric current is passed between, on the one hand, the contacts and, on the other hand, a counter electrode, the monomer is polymerised in the gap between the contacts. The properties of the polymer within the sensor is determined, not only by the monomer, but also by the counterion present in the monomer solution, which is incorporated into the polymer to balance the ionic charge of the polymer chain. Also the properties of the polymer are affected by the nature of the solvent in the original monomer solution.

Disclosure of the Invention

According to the present invention, there is provided a sensor capable of distinguishing between different enantiomers, which sensor comprises a pair of spaced-apart contacts and a semi-conductive polymer material spanning the gap between the contacts, which polymer material includes chiral sites.

The chiral sites in the polymer material may be formed by:

1. including optically active groups in the polymer, generally in a side group bonded to the chain; for example, when the polymer is polypyrrole, the chiral side chains may be bonded to one of the carbon atoms or to the nitrogen atom of the pyrrole ring in the oxidised polypyrrole;
2. incorporating an optically active counterion into the polymer material, for example by growing the polymer in the presence of such a counterion; examples of such counterions are menthoxy acetic acid, carzyl acetate and natural or synthetic chiral

amino acids such as cysteine and valine, or

3. growing the polymer from a monomer solution whose solvent is optically active.

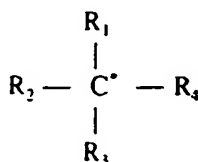
Although sensors as described in WO 93/03355 are capable of detecting aromas and the human nose is also capable of detecting aromas, the sensors themselves do not actually mimic the action of the nose since the sensors and the nose use completely different mechanisms for detecting aromas. The sensors detecting the conductivity of the polymer in the presence of the aromas while the human nose detects aromas because the aroma triggers nerve cells in the nose that the brain responds to. It is thus totally unexpected and surprising that the sensors can detect differences in enantiomers in this way, particularly since the physical properties of the enantiomers are identical to each other (apart from their effect on polarised light).

The polymer may be a copolymer.

Of the above three possibilities of including a chiral site, possibility 2 is preferred since it is easier to incorporate chiral counterions into the polymer material during the growth of the polymer chain than to incorporate such sites into the polymer itself, since steric effects can lead to problems in polymerising monomers having chiral sites. The use of optically active solvents in the monomer solution can give the desired discrimination between enantiomers, but it is less reliable than the use of optically active counterions and/or optically active sites in the polymer itself.

The optically active anionic counterion preferably includes a sulphonic acid (sulphonate) group since that stabilises the polymer material in air. The sulphonic acid group is preferably bonded directly to the optically active site although this is not an absolute necessity.

The counterion is preferably a compound of a general formula:



wherein R_1 , R_2 , R_3 and R_4 are all different and stand for different organic or inorganic substituents; preferably at least one of the substituents is or contains one or more sulphonate group(s) (although it is apparent that two or more of the substituents R_1 to R_4 cannot stand for sulphonate alone). Most preferred are commercially available optically active compounds, especially camphor sulphonic acid, which gives rise to the camphor sulphonate anion.

When the optically active site is included in the polymer chain, it is generally included in a side chain to the polymer backbone, for the reasons given above. Any

natural or synthetic optically active side group may be used so long as it can be introduced into the polymer chain. Example of such side groups are radicals formed from menthoxy acetic acid, carzyl acetate and natural or synthetic chiral amino acids such as cysteine and valine.

The chiral sites may be introduced into the polymer by an optically active solvent. In these circumstances, any suitable optically active solvent may be used.

The present invention also contemplates a method of detecting and discriminating between different chiral compounds, which comprises exposing a sensor of the type described above to a gaseous sample containing an optically active substance and measuring the resistance of the polymer material.

The present invention is not limited to the detection of aroma materials and can be used to detect gases and volatile materials that are odourless to the human nose. The gaseous sample may be the gas or vapour in the headspace above a volatile liquid or solid.

Brief Description of the Drawings

Figure 1 is a graph showing the signals (against time) from twelve sensors according to the present invention on exposure of the sensor to (S)-(+)-2-amino-1-butanol;

Figure 2 is a graph corresponding to Figure 1 when the same twelve sensors are exposed to (R)-(-)-2-amino-1-butanol;

Figure 3 is a graph showing the difference, for each sensor, between the signal of the sensor when exposed to (R)-(-)-2-amino-1-butanol as compared to the signal of the sensor when exposed to the (S) isomer, i.e. it is a plot of the difference between the graphs of Figures 1 and 2;

Figure 4 shows a plot of the difference in the signals of twelve sensors when exposed to (R)-(+)-limonene and (S)-(-)-limonene;

Figure 5 shows a polar plot of the signal from ten sensors exposed to (S)-(+)-carvone;

Figure 6 is a polar plot similar to Figure 5 but showing the response of twelve sensors of same type used in connection with the plot of figure 5 when exposed to (R)-(-)-carvone.

Figure 7 is a schematic view of three sensors of the present invention mounted on a common base.

Best Mode for Carrying out the Invention

Example 1

A substrate containing three sensors of the present invention is made in the manner disclosed in WO93/03355 (the content of which is incorporated herein by reference). The substrate (see Figure 7) includes a base 10 of silicon, alumina or silica on which there are deposited three pairs of contacts 14 (one pair for each sensor), the contacts of each pair being spaced apart by a gap 15 of approximately 10 μm . Electrical connections to the individual contacts 14 can be made by conductive pads 16. The whole of the substrate (except in the area of the pads 16 and in the area of a window 20 overlying both the gap 15 and adjacent areas of the contacts) is covered by a layer of an insulating stop-off material (not shown for ease of illustration). Details for the manufacture of the substrate are disclosed in WO93/03355.

25 ml of 0.1M (1R)(-)-10-camphor sulphonic acid solution (the solvent being deionised water) is measured into a beaker and 0.25 grams of purified pyrrole are added drop by drop using a teat pipette. The resulting pyrrole solution is stirred with a glass rod.

The substrate is immersed in the pyrrole solution so as to cover the window 20 where the polypyrrole will be grown. A saturated calomel reference electrode and a platinum gauze secondary (counter) electrode are also inserted into the solution. The contacts 14 of the substrate and the secondary and the reference electrodes are then all connected to a conventional potentiostatic circuit that maintains a potential of +850 millivolts between, on the one hand, the contacts 14 and, on the other hand, the reference electrode. This causes the pyrrole to polymerise in the window 20 of each sensor. After two minutes, the potentiostatic circuit is switched off and the polypyrrole grown on the substrate is allowed to equilibrate with the pyrrole solution for a further two minutes before being removed from the solution and rinsed with distilled water. The substrate is allowed to dry for 24 hours.

Example 2

The procedure described in Example 1 is followed except that the (1S)(+) enantiomer of camphor sulphonic acid is used instead of the (1R)(-) enantiomer.

Example 3

Six sensors of the type described in Example 1 and six sensors of the type described in Example 2 are mounted on a sensor head of a type commercially available from Neotronics Scientific Limited of Western House, 2 Cambridge Road, Stansted Mountfitchet, Essex, United Kingdom and each is connected to a circuit for measuring the resistance of the polypyrrole depos-

ited in the window 20. This involves applying a potential difference between the contacts 14 of each sensor so that an electrical current passes through the polypyrrole; the magnitude of the current flowing will give a measure of the resistance of the polymer. These sensors are then exposed to an atmosphere containing (S)-(+)-2-amino-1-butanol at a temperature of approximately 20°C and the resulting signals from the various sensors are shown in Figure 1 where the vertical axis is the sensor signal (i.e. change in resistance) and the horizontal axis denotes time in minutes. The sensors are then removed from the 2-amino-1-butanol atmosphere and allowed to equilibrate in dry air for a period of at least 5 minutes.

The sensors are then exposed to an atmosphere containing the (R)(-) enantiomer of 2-amino-1-butanol and the resulting signals from the sensors are shown in Figure 2.

It is apparent from the graph of Figures 1 and 2 that the two types of sensors are able to discriminate between the two enantiomers of 2-amino-1-butanol and also that the signals from the sensors of Example 1 give qualitatively similar signals to the two chiral gas samples as the sensors of Example 2, despite the polymers in the two sensors having opposite chiral sites.

The difference between the signal of each sensor when exposed to the (R)(-) enantiomer and the signal when exposed to the (S)(+) enantiomer is shown in Figure 3 which clearly shows that all the sensors are able to discriminate between the two enantiomers.

Example 4

A procedure similar to that described in Example 3 is repeated except that the sensors are exposed in turn to the two enantiomers of limonene. The resulting difference plot is shown in Figure 4.

It is clear from Figure 4 that the sensors are able to discriminate between the two enantiomers of limonene.

Example 5

The procedure of Example 1 was followed except that a racemic mixture of sodium camphor sulphonate was used instead of resolved (R)(-) camphor sulphonic acid.

Example 6

Ten sensors made by the procedure set out in Example 5 were exposed to the (S)(+)-carvone and the resulting steady-state signals from the sensors are shown in the polar plot of Figure 5.

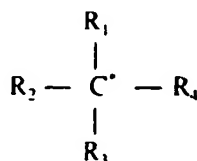
Twelve sensors of the same type were then exposed to (R)(-)-carvone and the resulting polar plot (on the same scale as in Figure 5) is shown in Figure 6.

It is clear from a comparison between Figures 5 and 6 that the sensors are able to discriminate between the two enantiomers of carvone. Note should be taken that

a polymer containing a racemic mixture of the counterion was still able to discriminate between the two enantiomers of carvone indicating that it is not necessary for all the sites in the polymer to have the same chirality in order to discriminate between different enantiomers.

Claims

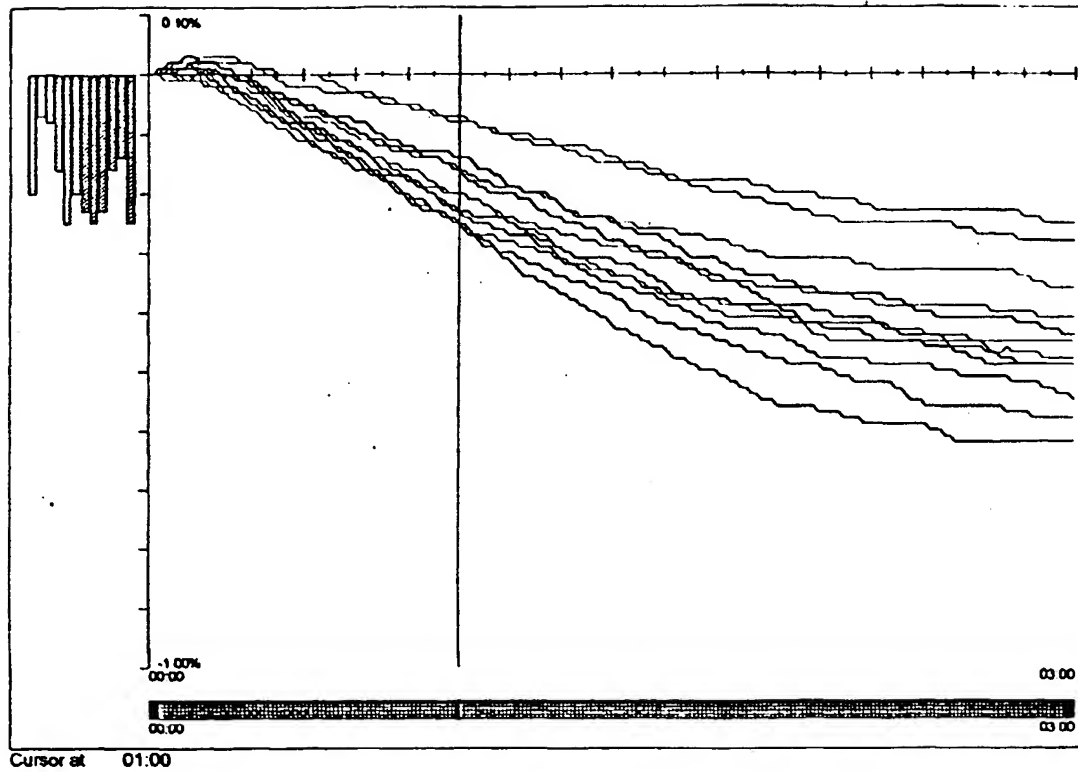
1. A sensor capable of distinguishing between different volatile enantiomeric substances in the gaseous phase, which sensor comprises a pair of spaced-apart contacts and a semi-conductive polymer material spanning the gap between the contacts, wherein the polymer material is such that its electrical resistance changes on exposure to volatile enantiomeric substances and wherein the polymer material includes chiral sites.
2. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are formed by a chiral counterion incorporated into the polymer material, for example by growing the polymer in the presence of such a counterion.
3. A sensor as claimed in claim 2, wherein the optically active anionic counterion includes a sulphonic acid (sulphonate) group.
4. A sensor as claimed in claim 3, wherein the sulphonic acid group is bonded directly to the optically active site.
5. A sensor as claimed in any one of claims 2 to 4, wherein the counterion is a compound of a general formula:



wherein R_1 , R_2 , R_3 and R_4 are all different and stand for different organic or inorganic substituents.

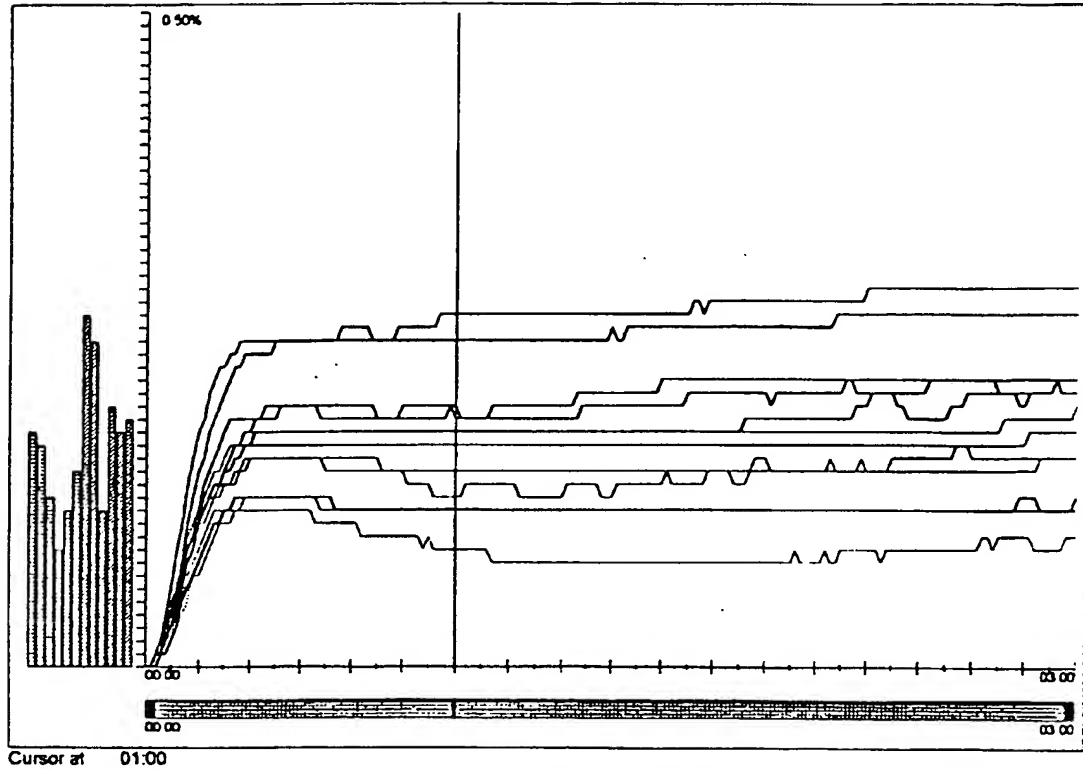
6. A sensor as claimed in claim 5, wherein at least one of the substituents R_1 , R_2 , R_3 and R_4 is or contains one or more sulphonate group(s).
7. A sensor as claimed in any one of claims any one of claims 2 to 6, wherein the counter-ion is camphor sulphonate, menthoxy acetate, carzyl acetate or natural or synthetic chiral amino acids, e.g. cysteine and valine.

8. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are formed by chiral side groups bonded to the backbone polymer chains, e.g. radicals formed from menthoxy acetic acid, carzyl acetate and natural or synthetic chiral amino acids such as cysteine and valine.
9. A sensor as claimed in claim 1, wherein the chiral sites in the polymer material are be formed by growing the polymer from a monomer solution whose solvent is optically active.
10. A method of detecting and discriminating between different chiral compounds, which comprises exposing a sensor as claimed in any one of claims 1 to 9 to a gaseous sample containing an optically active substance and measuring the resistance of the polymer material.



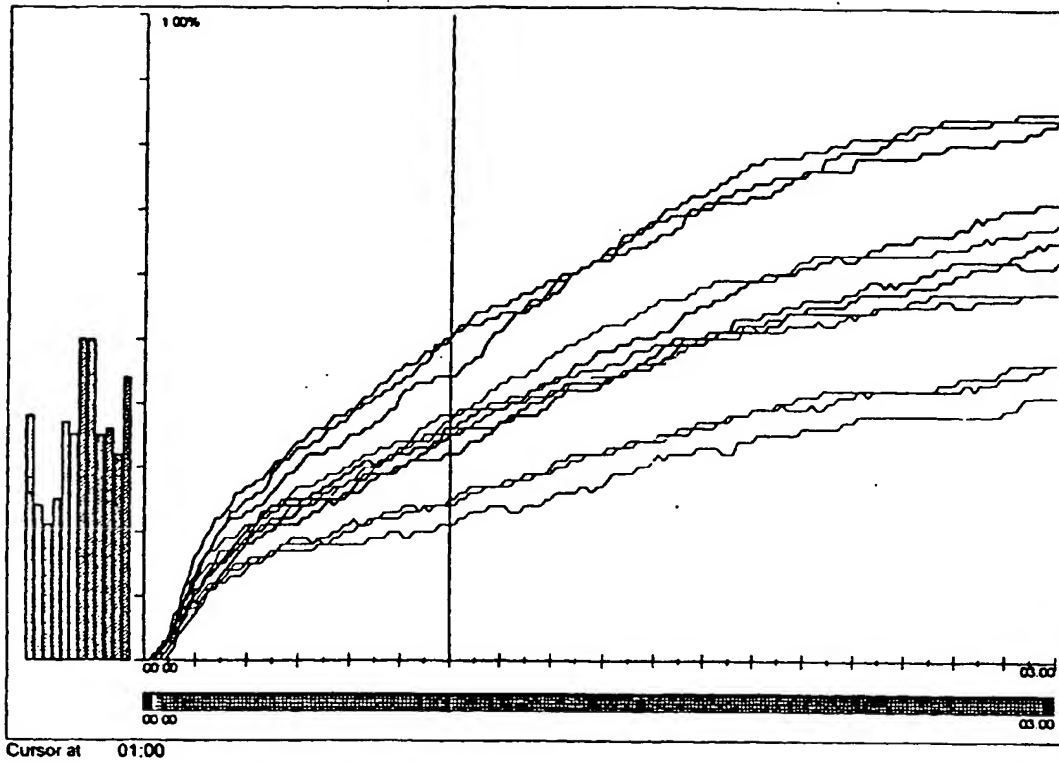
▣ -0.20% Type 298	▣ -0.07% Type 298	▣ -0.08% Type 298	▣ -0.16% Type 298
▣ -0.25% Type 298	▣ -0.20% Type 298	▣ -0.23% Type 297	▣ -0.25% Type 297
▣ -0.23% Type 297	▣ -0.16% Type 297	▣ -0.14% Type 297	▣ -0.25% Type 297

Figure 1



0.18% Type 298	0.17% Type 298	0.13% Type 298	0.09% Type 298
0.12% Type 298	0.15% Type 298	0.27% Type 297	0.25% Type 297
0.12% Type 297	0.20% Type 297	0.18% Type 297	0.19% Type 297

Figure 2



0.38% Type 298	0.24% Type 298	0.21% Type 298	0.25% Type 298
0.37% Type 298	0.35% Type 298	0.50% Type 297	0.50% Type 297
0.35% Type 297	0.36% Type 297	0.32% Type 297	0.44% Type 297

Figure 3

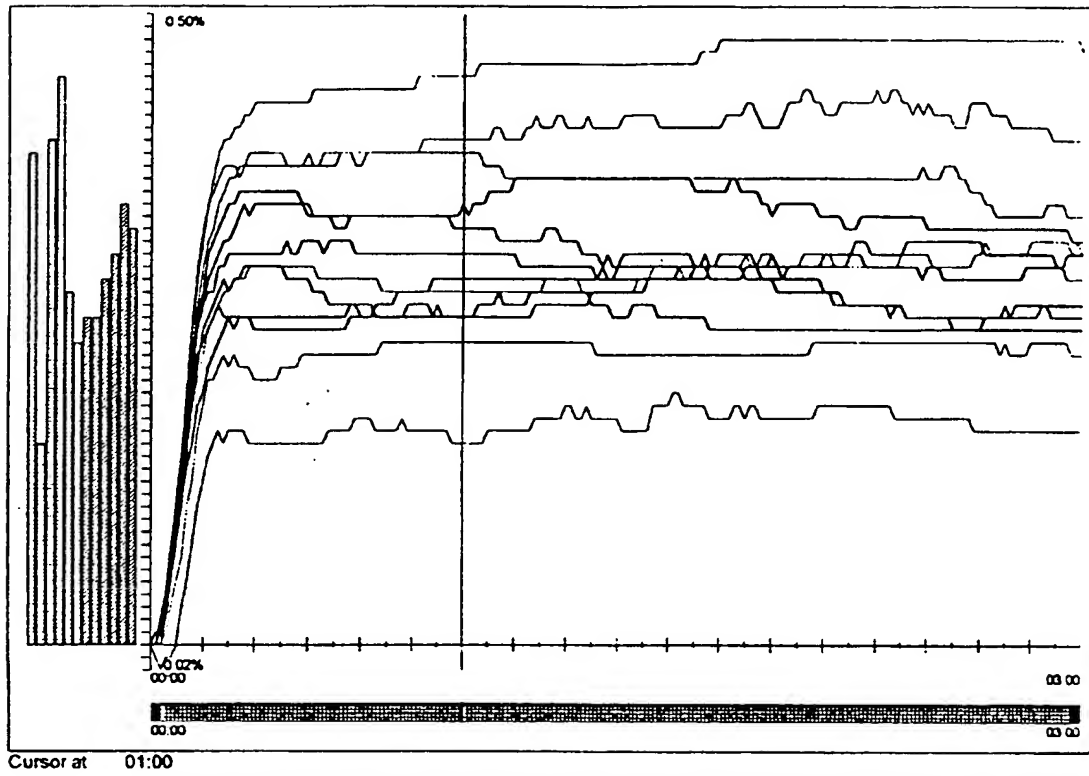


Figure 4

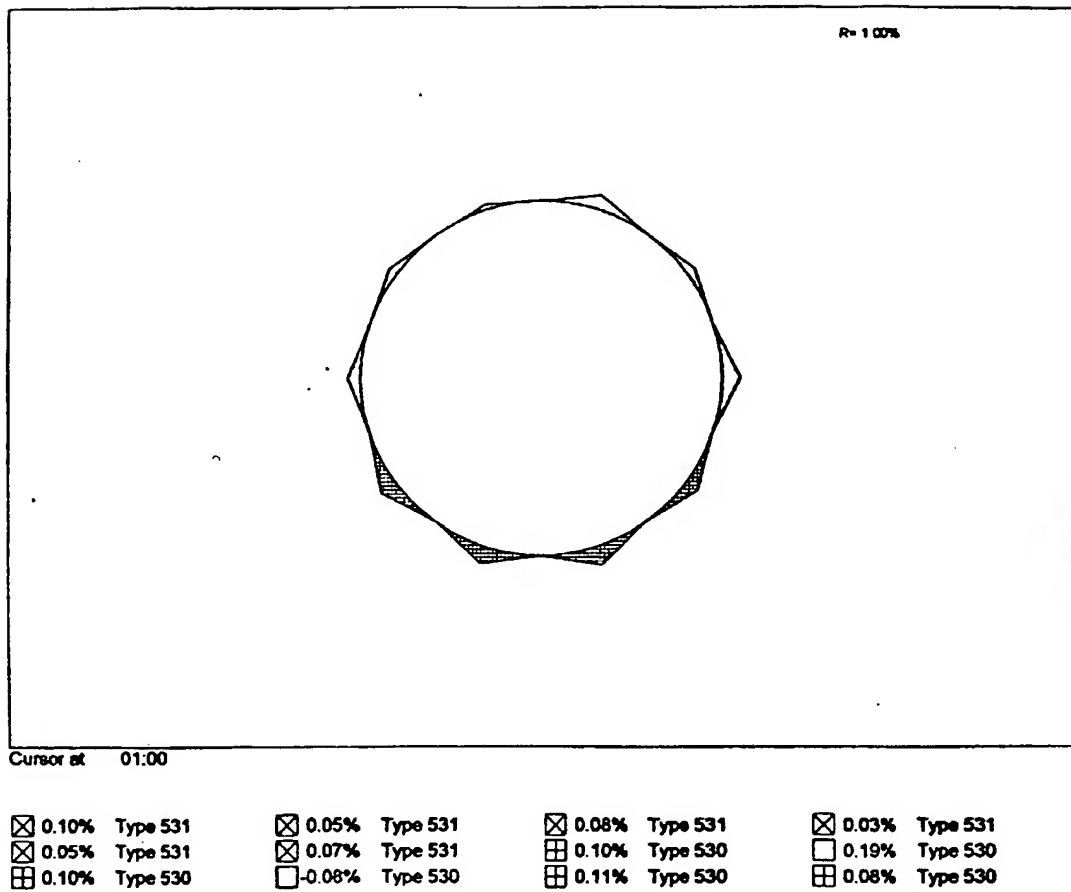


Figure 5

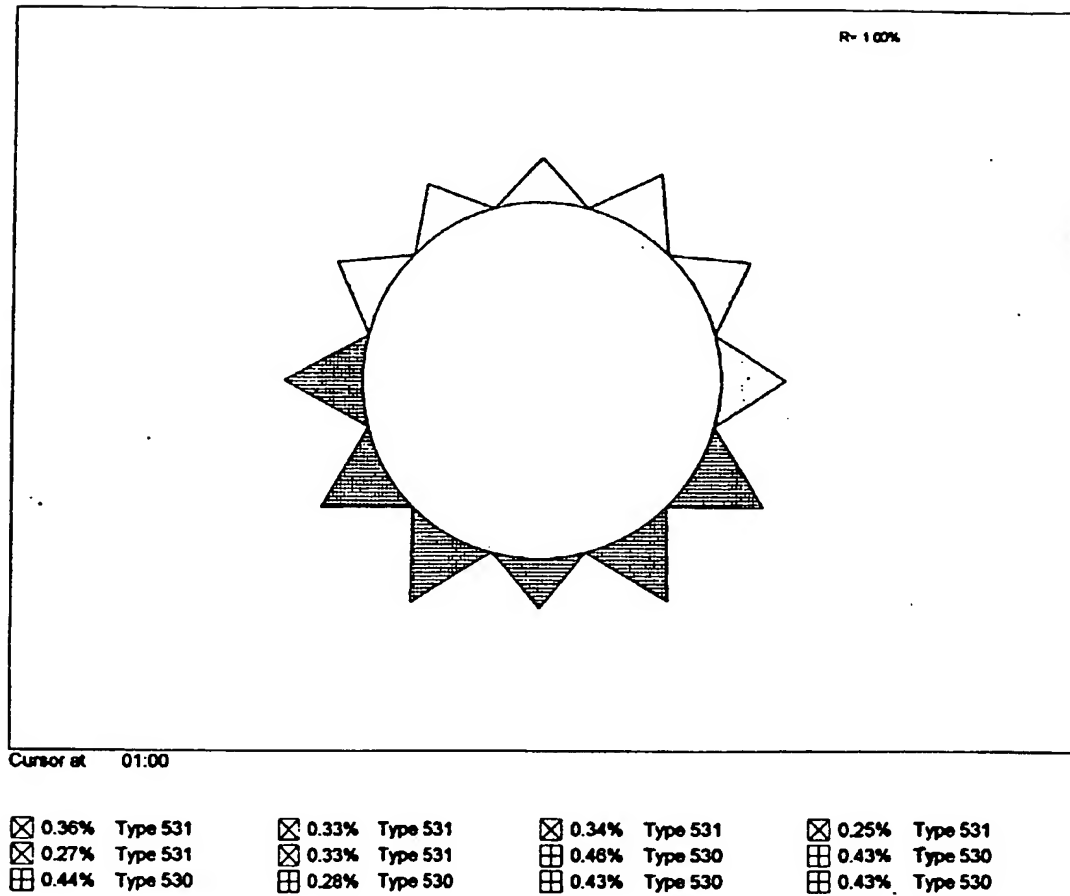


figure 6

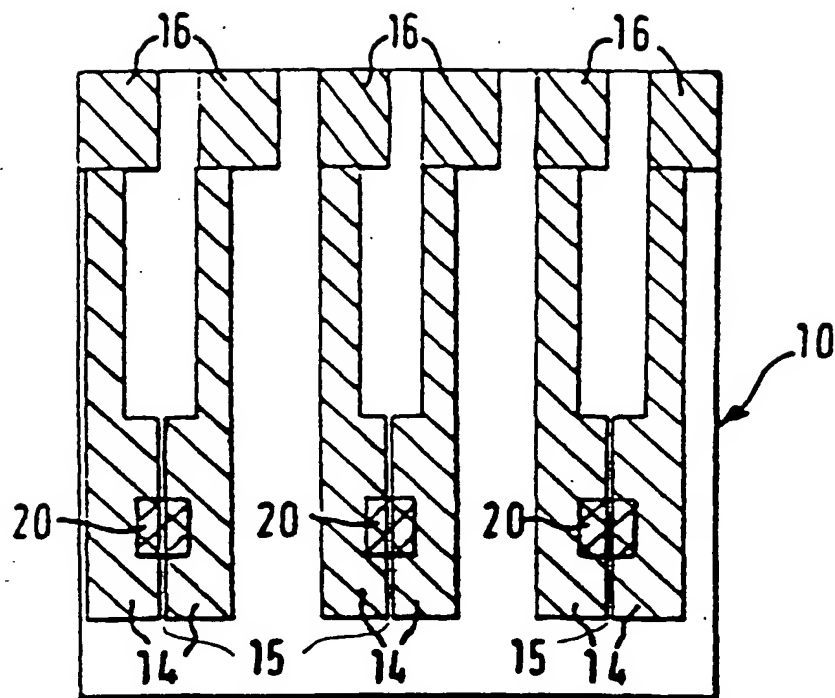


FIG. 7



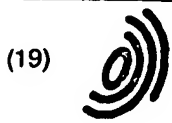
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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 1435

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	HELVETICA CHIMICA ACTA, vol. 70, no. 4, 1987, BASEL CH, pages 942-953, XP000674672 A. KARRER: "STRUCTURES AND ELECTRICAL PROPERTIES OF SOME NEW ORGANIC CONDUCTORS DERIVED FROM THE DONOR MOLECULE TMET" * abstract *	1	G01N27/12
A	GB 2 286 889 A (NEOTRONICS LTD.) * abstract *	1	
D,A	WO 93 03355 A (NEOTRONICS LTD.) * the whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G01N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 June 1997	Examiner Duchatellier, M
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(54) Composition containing polymer and conductive filler and use thereof

(57) A composition containing a polymeric matrix and a conductive filler component is provided. The conductive filler component comprises conductive particles and a polymer selected from the group consisting of substituted and unsubstituted polyanilines, substituted and unsubstituted polyparaphenylenes, substituted and unsubstituted polythiophenes, substituted and unsubstituted polyazines, substituted and unsubstituted polyparaphenylenes, substituted and unsubstituted polyfuranes, substituted and unsubstituted polypyrroles, substituted and unsubstituted polyselenophene, substituted and unsubstituted poly-p-phenylene sulfides and substituted and unsubstituted polyacetylenes, and mixtures thereof, and copolymers thereof.

Compositions of the present invention are useful as corrosion protecting layers for metal substrates, for electrostatic discharge protection, electromagnetic interference shielding, and as adhesives for interconnect technology as alternatives to solder interconnections.

In addition, films of polyanilines are useful as corrosion protecting layers with or without the conductive metal particles.

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Description

Technical Field

5 The present invention is concerned with polymeric compositions that are electrically conductive. In particular, the compositions of the present invention contain a polymeric matrix and a conductive filler component that includes conductive particles, such as metal particles and certain polymers.

The particular polymers employed, pursuant to the present invention, are the polyanilines, polyparaphenylenes, polythiophenes, polyfuranes, polypyrroles, polyselenophene, polyparaphenylenes, polyazines, poly-p-phenylene sulfides and polyacetylenes and mixtures thereof and copolymers made from the monomers to form the above polymers. Any of the above polymers can be substituted or unsubstituted.

Compositions of the present invention are especially useful as corrosion protecting layers for metal substrates, for electrostatic discharge protection, electromagnetic interference shielding, and as adhesives for interconnect technology to replace solder interconnections.

15 According to another aspect of the present invention, substituted and unsubstituted polyanilines are used as corrosion controlling layers for metal substrates.

Background of Invention

20 It has been suggested to convert normally insulating thermoset and thermoplastic polymers or prepolymers into electrically conducting compositions by admixing therewith various electrically conductive metal particles, such as silver and copper. The possible applications for such conducting compositions are quite extensive. For instance, it would be desirable to use these conducting compositions for electrostatic discharge protection, electromagnetic interference shielding, as adhesives for interconnect technology as replacements for solder joint connections.

25 However, there are problems associated with this technology. Often, high levels of the metal particles are needed to achieve the desired level of electrical conductivity, especially in high current carrying applications, such as interconnect technology, where the higher levels of electrical conductivity must be achieved. A loading level of 50% and higher is often required for such applications. A second serious problem with these metal fillers is that the more useful ones, silver and copper, tend to corrode in a variety of ambients. The metal has a tendency to oxidize, and thus, an oxidized layer of copper or silver will be on the surface of the particles, and will result in loss of conductivity, or at least a decrease in the conductivity.

Although both copper and silver are called "noble," they readily corrode in a variety of ambients. In oxygen saturated deionized water, copper and silver dissolve at a rate of about 0.2 $\mu\text{m/day}$, with no evidence of passivation. Both metals are susceptible to the presence of pollutants, notably chlorides and sulphur.

35 In the presence of humidity, pollutants and an applied electrical field (not an uncommon situation for the electronic parts in operation), copper and silver dissolve from the more positive metallic part and plate at the more negative part as dendrites. The formation of dendrites can result in electrical shorts that can lead to the failure of the electronic device.

Furthermore, with increasing line density and decreasing dimensions, ion accumulation alone, without dendrites, can ruin the designed electrical performance of the product. Use of inhibitors, such as benzotriazole (BTA), greatly improves the corrosion resistance of copper and silver. However, BTA is not very protective against dissolution at potentials above the open circuit potential, as it may occur in a galvanic contact with gold or platinum, or in service, with the applied field.

40 Moreover, to circumvent these problems, copper and silver metal particles are often coated with other more stable metals, such as gold or nickel. This is done by electroless or electroplating processes, which add additional processing costs and pose potential environmental concerns, due to the chemical make-up of the electroplating baths.

Summary of Invention

50 The present invention is concerned with a composition that comprises a thermoset or thermoplastic polymeric matrix, and a conductive filler component. The conductive filler component contains conductive particles and certain polymers. The polymer is selected from the group consisting of polyparaphenylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophene, polyparaphenylenes, polyacetylenes and mixtures thereof, and copolymers thereof. These polymers can be substituted or unsubstituted. In addition the conductivity of these polymers can be tuned from about $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ to about $10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$ by chemical manipulation such as by incorporation of substituents, doping levels and/or processing conditions. These polymers are also referred to hereinafter as "conducting" or "conductive" polymers.

55 In addition, the present invention is concerned with the use of the above disclosed compositions, as corrosion protecting layers for metal substrates, for electrostatic discharge protection, electromagnetic interference shielding and as adhesives for interconnections as alternatives to solder interconnections. The present invention provides for a simple,

relatively inexpensive and environmentally safe method of protecting the metal particles from corrosion, without loss in electrical conductivity. Moreover, the present invention makes it possible to reduce the loading level required for the metal particles.

It has also been found, pursuant to the present invention, that polyanilines and especially alkoxy substituted polyanilines, as such, can be used as corrosion protecting layers for metal substrates.

Summary of Drawing

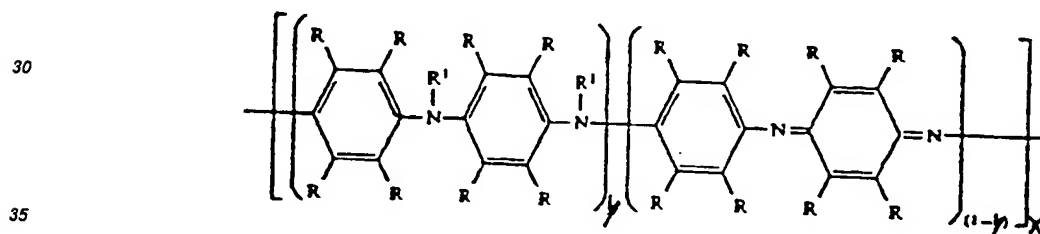
Figure 1 provides potentiodynamic polarization curves for copper coated with different materials.

Best and Various Modes For Carrying Out Invention

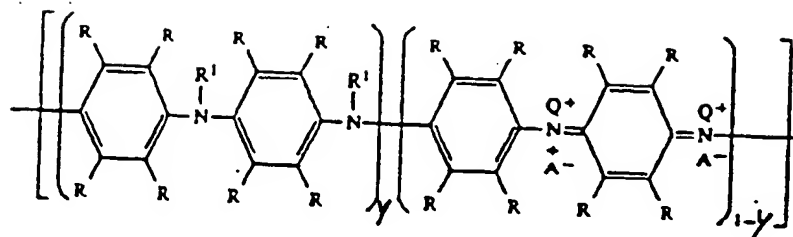
The filler component of the compositions of the present invention contain electrically conductive particles, and a certain amount of a conducting polymer. The particles are preferably carbon and metal, such as silver or copper, and in the form of powder, flakes or fibers.

The polymer portion of the filler component is selected from substituted and unsubstituted polyparaphenylenes, substituted and unsubstituted polyazines substituted and unsubstituted polyanilines, substituted and unsubstituted polythiophenes, substituted and unsubstituted polyfuranes, substituted and unsubstituted polyparaphenylenes, substituted and unsubstituted poly-p-phenylene sulfides, substituted and unsubstituted polypyrroles, substituted and unsubstituted polyselenophene, substituted and unsubstituted polyacetylenes, and combinations thereof and copolymers made from the monomers to form the above polymers. Examples of suitable substitutions include alkyl, aryl, alkoxy aryloxy groups, alkanyl and aralkyl. Typically, such groups contain 1-12 carbon atoms. The substituted polymers are preferred because they exhibit enhanced solubility and processability.

One type of polymer useful to practice the present invention is the conductive form of a substituted or unsubstituted polyaniline having the following general formula:



wherein each R can be H or any organic or inorganic radical; each R can be of the same or different; wherein each R¹ can be H or any organic or inorganic radical, each R¹ can be the same or different; X is ≥ 1 and preferably $X \geq 2$ and y has a value from 0 to 1. Examples of organic radicals are alkyl or aryl radicals. Examples of inorganic radicals are Si and Ge. This list is exemplary only and not limiting. The most preferred embodiment is emeraldine base form of the polyaniline, wherein y has a value of 0.5. In the above equation, the polyaniline is in the non-doped form having a conductivity of about $10^{-10} \text{ohm}^{-1} \text{cm}^{-1}$. The polyaniline can be converted to the conducting form by doping, which involves reacting the polyaniline with a cationic species QA. QA can be, for example, a protic acid, wherein Q is hydrogen. The nitrogen atoms of the imine part of the polymer become substituted with the Q cation to form an emeraldine salt, as shown in the following equation:



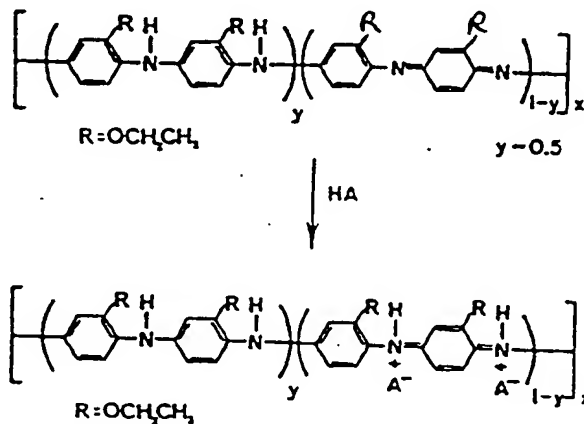
The emeraldine salt is the highly conducting form. The conductivity of the polyaniline can range from $10^{-10} \text{ohm}^{-1} \text{cm}^{-1}$ (characteristic of the base and non-doped form) to about $10^3 \text{ohm}^{-1} \text{cm}^{-1}$ upon full doping.

The ring substituted polyaniline, and in particular, the ortho-ethoxy derivatives, and ortho propyl derivatives exhibit appreciably greater solubility than the unsubstituted ones.

The unsubstituted emeraldine base form of polyaniline is soluble in various organic solvents, and in various aqueous acid solutions. Examples of organic solvents are dimethyl-sulfoxide (DMSO), dimethylformamide (DMF) and N-methylpyrrolidinone (NMP). This list is exemplary only and not limiting. Examples of aqueous acid solutions is 80% acetic acid, and 60-88% formic acid. This list is exemplary only and not limiting.

The ring substituted derivatives are also soluble in more solvents, including less polar solvents such as chloroform, methylenechloride, xylene and toluene.

Preferred polyaniline compounds in the present invention are ethoxy derivatives, represented by the following:



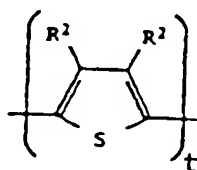
The ethoxy substituted polyaniline in the non-doped form (base) can be readily dissolved to a 10% by weight solution in NMP, and spun at various rpms to form films of different thicknesses (184,339 and 477 nm, respectively). Films from this polymer are very homogenous and well adherent. Even the thinnest film behaves as a perfect barrier to oxygen, as electrochemical data show no current normally attributable to oxygen reduction. The measured cathodic current of about $2 \times 10^{-7} \text{A/cm}^2$ is independent of film thickness, type of metal (copper, silver and platinum) and ambient atmosphere (air and nitrogen). The current is diffusion limited and most likely caused by reduction of ethoxy radical or the ethoxy polymer backbone. The anodic current, metal dissolution, is in all cases greatly reduced by a factor which increases with film thickness. The protection is substantial, in particular at high potentials, where Cu dissolution (and similarly silver dissolution) is about 4 orders of magnitude lower than measured on unprotected metals.

In addition, ethoxy substituted polyaniline spin-doped with acid HA, such as hydrochloric acid, can be prepared by first spin-coating of the polymer in the non-conducting form, and subsequently doping such as by dipping the film into a 1 N aqueous hydrochloric acid solution for about 1 hour and then drying. The polymer upon full doping has a conductivity on the order of $10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$. Its corrosion protection is similar to that offered by non-doped ethoxy-polyaniline, except for the measurement of the oxygen reduction rate. Apparently, as the polymer is conducting, it allows a passage of electrons needed for oxygen reduction. The protection of the film is excellent, especially at anodic potentials.

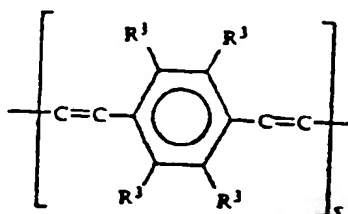
Examples of another substituted polyaniline is ortho-propyl polyaniline.

The polyanilines, and preferably the alkoxy substituted polyanilines, such as ethoxy substituted polyanilines, as such, both in the non-doped less conducting form and the doped more conducting form, are useful as corrosion protecting layer on a metal substrate. The polyanilines are preferably employed in their conducting doped form.

Examples of suitable polythiophenes are represented by the following formula:



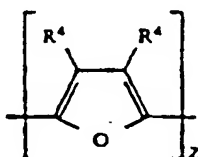
wherein each R^2 is H or any organic or inorganic radical; wherein $t \geq 1$ and preferably wherein at least one R^2 is not H. Polyparaphenylenevinylenes useful to practice the present invention have general formula wherein each R^3 is H or any organic or inorganic radical, and wherein $s \geq 1$. Each R^3 can be the same or different:



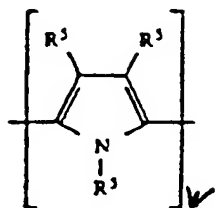
Polyazines useful to practice the present invention have general formula wherein R^{10} is H or an organic or inorganic radical:



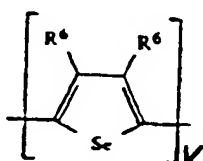
Polyfurans useful to practice the present invention have general formula, wherein $Z \geq 1$ and each R^4 is H or any organic radical, and each R^4 can be the same or different:



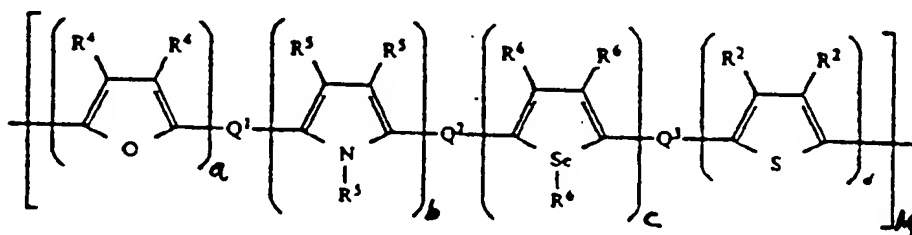
Polypyrroles which are useful to practice the present invention have general formula, wherein $w \geq 1$, each R^5 is H or any organic or inorganic radicals; wherein each one R^5 can be the same or different:



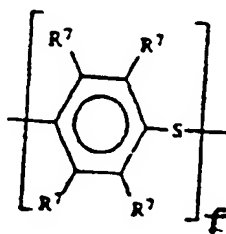
Polyselenophene useful to practice the present invention have general formula, wherein $v \geq 1$, and each R^6 is H or any organic or inorganic radical and wherein each R^6 can be the same or different:



Examples of combinations of polythiophenes, polyfurans, polypyrroles and polyselenophene useful to practice the present invention are represented by the following equations wherein R^4 , R^5 and R^6 are as defined above wherein at least two of a, b, c and d are greater than or equal to 1; $m \geq 1$; Q^1 , Q^2 , Q^3 can be a vinylene group or a direct bond between adjacent constituents:



Poly-p-phenylene sulfides useful to practice the present invention are represented by the following general formula wherein each R^7 is H or any organic or inorganic radical and $f \geq 1$, each R^7 can be the same or different:



The article entitled New Routes to Processed Polyacetylenes, T. Swager, et al. Polymer Preprints, Vol. 30, No. 1, p. 161, April 1989, describes methods of preparing polyacetylene from a soluble precursor, the teaching of which is incorporated herein by reference.

The conductive particles can be precoated with the above conducting polymers prior to admixture with the polymeric matrix. In the alternative, the above conducting polymer and conductive particles can be separately admixed with the polymeric matrix. The blending can be carried out by dispersion or more preferably, by solution blending.

When the above defined conducting polymer and conductive particles are admixed with the polymeric matrix, lower amounts of conductive particles are needed to obtain a given conductivity.

When used to precoat the conductive particles, the conducting polymer is generally used to provide coatings about 0.1 to about 5 microns thick, and preferably about 0.15 to about 2.5 microns thick.

The particles can be solution coated.

The polymeric matrix employed, pursuant to the present invention, can be thermoset or thermoplastic polymeric materials. The preferred polymers are the polyepoxides, polyacrylates, polymethacrylates, polysiloxanes, and polyimides, such as the polyimide siloxanes, polyurethanes, polyolefins, and polyamides. Mixtures of polymers as well as copolymers can be employed when desired.

The composition of the matrix polymer, the conducting polymer and the conducting particles is as follows: The conducting polymer is typically employed in amounts of 0.3 to about 90, and preferably about 0.5 to about 50% by weight, and most preferably about 1 to about 10% by weight based upon the total weight of the polymeric matrix.

The amount of conducting particles is typically about 40% to about 95% by weight, preferably about 75 to about 95% by weight, and most preferably about 80 to about 90% by weight relative to the total polymer content (conducting polymer and matrix polymer).

The compositions of the present invention when used as a corrosion prevention layer are typically employed at thicknesses of about 500 Å to about 5 µm, and preferably about 1000 Å to about 5000 Å. The substrates employed are typically copper and silver.

The compositions of the present invention can be used to bond together a semiconductor with a substrate as a replacement for solder interconnections.

The compositions of the present invention are useful as electromagnetic interference (EMI) coatings on a dielectric surface. For example, electrical components are frequently contained within dielectric housings, such as cabinets, molded plastics and the like. To reduce the susceptibility of the electronic components contained within the housing to electromagnetic radiation, the dielectric housing can be coated with the compositions of the present invention.

The following non-limiting examples are presented to further illustrate the present invention:

Example 1 - Preparation of Polyanilines

Polyaniline (unsubstituted) was prepared by the chemical oxidative polymerization of aniline in aqueous/1 normal hydrochloric acid using ammonium persulfate as the oxidant. The conducting polyaniline hydrochloride salt is isolated from the reaction mass. The HCl salt is converted to the polyaniline base form (non-conducting) by reacting with 0.1M NH₄OH. The isolated polyaniline base can then be doped with the desirable acid or alkylating agent to give a conducting derivative.

The substituted polyaniline derivatives were prepared by the oxidative polymerization of the appropriate ring-substituted aniline monomer along the lines of the method described. For example, the ethoxy-substituted polyaniline was prepared by the oxidative polymerization of o-phenetidine. The ethoxy-polyaniline hydrochloride salt and base form were isolated as described above.

The conducting ethoxy polyaniline doped with toluene sulphonic acid was prepared by reacting the ethoxy polyaniline base powder heterogeneously with 1 normal aqueous toluenesulfonic acid. It can also be prepared by reacting a solution of ethoxy-polyaniline base in NMP or gamma-butyrolactone with toluenesulfonic acid.

Alternatively, o-phenetidine can be polymerized in the presence of aqueous 1 normal toluene sulfonic acid instead of hydrochloric acid to yield the conducting ethoxy polyaniline tosylate.

The ethoxy-polyaniline tosylate is dissolved in NMP (N-methyl pyrrolidinone) or gamma-butyrolactone to prepare 6 weight % solutions.

Example 2 - Preparation of Coated Silver Particles

An Ethoxy polyaniline tosylate solution prepared in Example 1 was added to the silver particles. The particles were stirred in the conducting solution. The particles were then filtered and dried under vacuum.

Example 3 - Preparation of Conductive Composition

A conductive paste is made by combining the polyaniline coated silver powder of Example 2 with the host polymer, such as polymethylmethacrylate in an appropriate solvent system, such as xylene. The solvent is chosen so as not to dissolve the polyaniline. The materials are blended by a dispersion technique or high shear mixing.

Example 4 - Blending of a Host Polymer and Polyaniline and Metal Fillers

To a host resin, in particular, polymethylmethacrylate in gamma-butyrolactone was added a gamma-butyrolactone solution of the ethoxy polyaniline tosylate. The two polymers mixed well. To the polymer blend solution were added silver particles, by dispersion mixing. The resulting mixture was used to spin-coat conducting coatings. The mixture can also be processed by conventional means to fabricate conducting films or composites suitable for the uses disclosed above.

Example 5

Corrosion was measured in two complementary ways. The first water drop test 1 uses an electrochemical technique described as follows:

Evaluation of the corrosion rate by electrochemical techniques is direct and precise, but not readily applicable to conditions of atmospheric corrosion. Tests were conducted in a miniature cell, that was designed in an attempt to bridge the benefits of electrochemical testing and the challenges presented by corrosion reactions under a thin layer of an electrolyte. The cell can use a droplet of water as an electrolyte, as described by Brusic, et al., J. Electrochem. Soc., 136 42 (1989).

The set-up consists of the sample (working electrode) masked with plating tape to expose a 0.32 cm² area. Pt mesh (counter electrode), and a mercurous sulfate electrode (reference electrode), with a filter paper disk separating each electrode. The procedure was as follows: The metallic sample, with or without polyaniline coating, was placed on a small jack, and the working area, covered with a tightly fitted filter paper and a flat Pt mesh, was maneuvered into a center of the opening of a vertically positioned and a rigidly held Beckmann fitting. The inner diameter of the fitting was 8 mm, i.e., large enough to easily expose the entire working area that has a diameter of 6.4 mm. The sample was then raised and kept in place at a hand-tight pressure against the fitting. The second filter disk was an Eppendorf pipette, and the reference electrode was positioned over the sample using the fitting as a holder. A typical droplet size was 20 μ l. Due to small distances between the electrodes, the ohmic resistance in the cell was relatively small even with electrolytes such as deionized and triple-distilled water. As the ohmic resistance of the cell was only about 800 in the first seconds of measurement, insignificant errors in the evaluation of corrosion rates are introduced. The procedure was to monitor the corrosion potential for about 15 minutes and periodically measure the polarization resistance by scanning the potential \pm 20 mV from the corrosion potential at 1 mV/s. The corrosion rate was calculated using the Model 352 SoftCorr II software by AG&G Princeton Applied Research. The potentiodynamic polarization curve was then measured at a rate of 1 mV/s from 0.25 V cathodic of the corrosion potential. The corrosion rate was evaluated by an extrapolation of the cathodic and anodic currents to the corrosion potential.

Excellent corrosion protection has been measured with unsubstituted, undoped polyaniline base, Figure 1 (curve 3). The film was processed from a 5% solution in NMP, and baked after spin-drying at 80°C for 4 minutes. Its conductivity is low, 10^{-10} ohm⁻¹cm⁻¹, and thermal stability is up to > 400°C. The film adheres well to the metal surface and acts as a barrier to all corrosion reactions. Potentiodynamic current-potential curve looks similar to one obtained on unprotected copper, but the corrosion current is lower and the corrosion potential higher for copper covered with this film. This indicates that the film also affects exodus of copper ions, i.e., the anodic reaction.

The surprisingly effective protection is observed with ethoxy substituted non-doped polyaniline base, Figure 1 (curve 1). This polymer is applied from a 10% solution in NMP, and spun at various rpms to form films of different thicknesses (184, 339 and 477 nm, respectively). The films are very homogenous and well adherent. Even the thinnest film behaved as a perfect barrier to oxygen, as electrochemical data show no current normally attributable to oxygen reduction. The measured cathodic current of about 2×10^{-7} A/cm² is independent of film thickness, type of metal (copper, silver and platinum tested) and ambient atmosphere (air and nitrogen tested). The current is diffusion limited and most likely caused by reduction of ethoxy radical or the ethoxy polymer backbone. The anodic current, metal dissolution, is in all cases greatly reduced by a factor which increases with film thickness. The protection is substantial, in particular at high potentials, where Cu dissolution (and similarly silver dissolution) is about 4 orders of magnitude lower than measured on unprotected metals.

Ethoxy substituted polyaniline doped with hydrochloric acid was prepared by spin-drying the non-doped ethoxy base polyaniline and then doping by dipping into 1N hydrochloric acid. The doped polymer has a conductivity on the order of 10^{-2} ohm⁻¹cm⁻¹. Its corrosion protection is similar to the one offered by the non-doped ethoxy-polyaniline base, except for the measurement of the oxygen reduction rate. Since the doped polymer is more highly conducting, it allows a passage of electrons needed for oxygen reduction. The protection of the film is excellent, especially at anodic potentials.

The second method:

Water Drop Test II:

A drop of water is placed across adjacent metal leads. A potential of 5V is then applied across the metal lines and failure or time for dendrite formation is measured. The time is given from the time the voltage was applied until shorting between the lines is observed.

Test vehicle for measurement:

Test vehicle: Cu lines applied by evaporation on .5 μm SiO₂ coated wafers. Copper line patterns include: 1) line width--8 mils spacing--16 mils 2) line width--6 mils spacing 12 mils.

10 Bare Copper (Cu)

The copper lines were cleaned with a 1.5% acetic acid solution to remove native oxides, rinsed with deionized water and dried.

Results are as follows:

15 3 repeated test measurements:

16 mils spacings--45 seconds, 48 secs, 51 secs for dendrites to form

12 mils spacings--39 seconds, 42 secs, 40 secs for dendrite to form

Copper Lines Treated with Benzotriazole (BTA) Solution

Copper was dipped in 1.5% acetic acid, rinsed with DI water; while the copper was still wet, it is dipped in mildly alkaline KOH solution (pH \approx 10) for 10 minutes. This results in formation of Cu₂O (about 2 nm thick). This is followed by a water rinse. The sample is then dipped into a BTA solution for 10 minutes (1 g BTA/1 liter H₂O), rinsed and dried.

For both copper and silver lines (same width and spacings) immediate dendrite formation occurred with the water drop test for both bare surfaces and BTA coated surfaces.

25 Ethoxy polyaniline (base or non-conducting form)

A 10% weight solution in NMP of the ethoxy polyaniline base was used to spin-coat films on wafers with copper and silver lines (as described above). Spinning at 3000 rpm/30s and softbaking 85°C for 5 minutes resulted in a 5159 Å thick film.

30

Water Drop Test After 220°C/30 Minutes Storage

Copper and silver lines with the 5159 Å ethoxy-polyaniline film did not form any dendrite, even after 30 minutes (water drop test).

35

Temperature and Humidity Test (85°C, 80% relative humidity)

The 5159 Å thick film of the ethoxy non-doped polyaniline base coated silver and copper surfaces were tested under the above temperature and humidity conditions. Test results for both silver and copper show that after 1076 hours storage at the above T:H conditions, no dendrites formed even after 30 minutes in the Water Drop II Test. This is both for the 12 mils and 16 mils lines.

40

Temperature/Humidity/Bias Voltage Test

Leakage current is continually monitored and failure is flagged when the isolation resistance reading between the 2 lines is less than 16 mega-ohms. Test is done while wafer is in the oven at 85°C and 80% relative humidity. The copper and silver line pattern used were a) 8 mils wide 16 mils spacings and b) 6 mils wide 12 mils spacings. The applied voltage was 3 volts and 14.99 volts. The polyaniline coated wafers passed 500 hours and 1000 hours.

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Ethoxy Polyaniline Doped With Hydrochloric Acid (more highly conducting Form of Polymer)

a. thickness of the coating was 5000 Å. Room temperature water drop test results: No dendrite formation even after 30 minutes (similarly to the base form) Example 5.

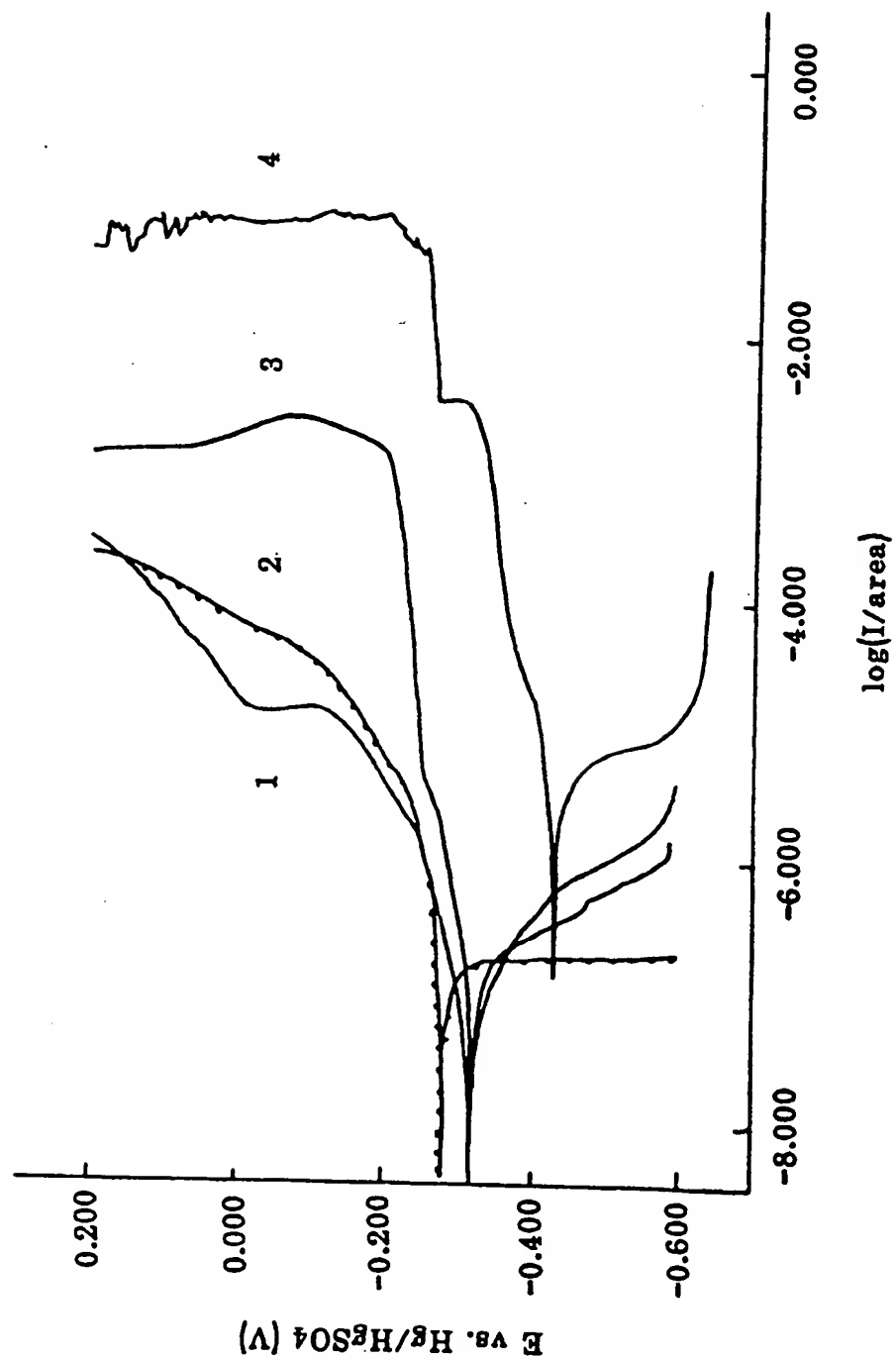
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b. Temperature/humidity storage (85°C for 1016 hours). Water drop test results showed no dendrite formation even after 30 minutes test.

Claims

1. A composition comprising a thermoset or thermoplastic polymeric matrix, and a conductive filler component, wherein said filler component comprises at least one conducting polymer selected from the group consisting of substituted and unsubstituted polyparaphenylenevinylenes, substituted and unsubstituted polyanilines, substituted and unsubstituted polyazines, substituted and unsubstituted polythiophenes, substituted and unsubstituted polyparaphenylenes, substituted and unsubstituted poly-p-phenylene sulfides, substituted and unsubstituted polyfuranes, substituted and unsubstituted polypyrroles, substituted and unsubstituted polyselenophene, substituted and unsubstituted polyacetylenes and mixtures thereof; and copolymers thereof; and conductive particles.
2. The composition of claim 1 wherein the amount of said conducting polymer is about 0.3 to about 90% by weight of the total of said polymeric matrix.
3. The composition of claims 1 to 2 wherein the amount of conductive particles is about 40 to about 95% by weight based upon the total of said conducting polymer and said polymeric matrix.
4. The composition of any of the preceding claims 1 to 3 wherein said polymeric matrix comprises at least one polymer selected from the group consisting of polyepoxides, polyacrylates, polysiloxanes and polyimides, polymethacrylates, polyurethanes, polyolefins, and polyamides.
5. The composition of any of the preceding claims 1 to 4 wherein said particles are silver or copper.
6. The composition of any of the preceding claims 1 to 4 wherein said conductive particles are precoated with said conducting polymer.
7. The composition of any of the preceding claims 1 to 6 wherein said polymer is a polyaniline, comprising an alkoxy substituted polyaniline.
8. The composition of any of the preceding claims 1 to 7, wherein said composition is in the form of a paste.
9. The composition of any of the preceding claims 1 to 8 wherein said conducting polymer has conductivity of about $10^{-10}\text{ohm}^{-1}\text{cm}^{-1}$ to about $10^6\text{ohm}^{-1}\text{cm}^{-1}$.
10. A composite comprising a metal substrate, wherein said metal comprises copper or silver and as a corrosion protecting layer on at least one major surface of said substrate, a composition according to any one of the preceding claims 1 to 9, or a layer of a polyaniline, comprising an alkoxy polyaniline or an ethoxy polyaniline.
11. A method for providing electrostatic discharge protection or electromagnetic interference shielding by applying the composition of any of the preceding claims 1 to 9.

FIG. 1



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